

Ex-Situ Accelerated Stress Tests of Pt/C Cathode Catalysts. The Importance of Standard Test Procedures

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Proton Exchange Membrane Fuel Cells (PEMFCs) are considered as possible alternatives to Internal Combustion Engines (ICEs) for automotive applications. PEMFC generates electrical energy by converting chemical energy (Hydrogen and Oxygen) with the only reaction product being water. Moreover, the efficiency of PEMFC is very high compared to ICE. The impending fossil fuel depletion and the need to reduce greenhouse effect gases emission have thus driven the ongoing global research aimed at developing PEMFC systems to replace ICEs.

However, PEMFC commercialization is still limited mainly due to the high price of the components and the durability of the Cathode Catalyst Layer (CCL). Indeed, in order to replace ICEs, PEMFCs should exhibit equivalent lifetime (around 5,000 hours). During operation the cathode potential usually oscillates from 0.9 V (idle) to 0.6 V (peak power) but can also reach up to 1.5 V during startup/shutdown, which leads to a strong degradation of the catalyst and decrease in PEMFC's performances. Accelerated Stress Tests (AST) which can be performed on real PEMFC systems (*in-situ*) or using an electrochemical cell with liquid electrolyte (*ex-situ*) is used to study the catalyst durability. ASTs usually consist in a large number of potential cycles (at high frequency) to simulate cathode operation, the Electrochemical Active Surface Area (ECSA) is then measured in course of test to monitor catalyst changes. *Ex-situ* AST are mostly used because of the cost of an *in-situ* test and also to avoid any interferences on the failure mechanisms due to other PEMFC's components degradation (mainly the membrane and gas diffusion layer) [1, 2].

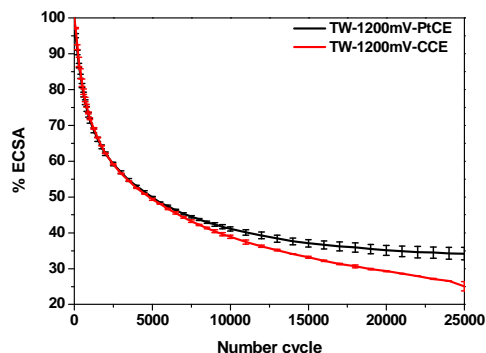


Figure 1: ECSA loss during successive TWs from 0.6 to 1.2 V at 120 mV sec⁻¹ in 0.1 M HClO₄ using a Pt or a C counter electrode

We present here studies on the effect of experimental protocols on the ECSA loss rate, specifically inadvertent mass contributions of the Pt counter electrode (PtCE) and the frequency of low potential (0.02 V) ECSA assessment. During high temperature testing, it was found that the dissolution of the PtCE resulted in the increase in ECSA after 10,000 cycles. During these multiple anodic/cathodic cycles, the counter electrode potential is not controlled and was found to lead to mass dissolution, as was confirmed by transmission electron microscopy and detection of Pt in the electrolyte solution using

Inductively Coupled Plasma/Mass spectroscopy (ICP/MS). Figure 1 presents the ECSA evolution in course of multiple triangular wave (TW) at 120 mV sec⁻¹ to 1.2 V using a PtCE or a Carbon counter electrode (CCE). The results show that the ECSA decay is the same during the first 5,000 cycles, but then the AST using a PtCE electrode exhibits a slower decrease and reaches a plateau. The ICP/MS results obtained indicate that the final Pt concentration in the electrolyte exceeds the theoretical maximum concentration which indicates a contribution from PtCE material dissolution.

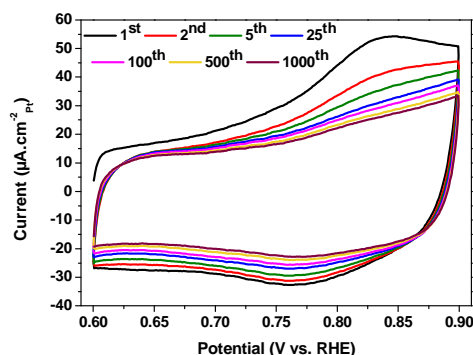


Figure 2: Isolated I-E curves recorded in course of 1,000 consecutive TW perturbations, 0.6 to 0.9 V at 60 mV sec⁻¹

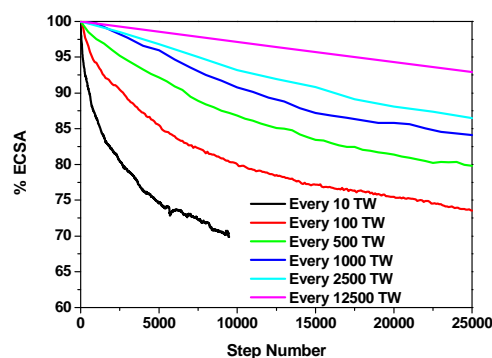


Figure 3: ECSA loss during multiple TWs (0.6 to 0.9 V at 60 mV sec⁻¹) as a function of the ECSA measurement frequency

Here we also present a correlation of the increase frequency of ECSA assessment with increased ECSA loss. The effect of the frequency of the ECSA assessment has to our knowledge not yet been presented in literature. Within this study the TW perturbation signal (for a UPL of 0.9 V) during consecutive cycles clearly reveals a low reversibility of the oxidation/reduction due to high scan rate (60 mV sec⁻¹) and limited lower potential limit (0.6 V) as presented in the Figure 2. Different experiments also indicate that the oxide layer generated during consecutive TW strongly depends on the number of repetitive perturbation showing two reduction peaks upon this first scan below 0.6 V. During ECSA measurement, the potential is lowered enough to allow the full reduction of the oxide layer. As shown in Figure 3, ECSA frequency can greatly affect the loss rate ranging from less than 10% after 25,000 cycles for ECSA measured every 12,500 cycles to 30% loss after only 10,000 steps when the frequency is increased to every 10 cycles.

References:

- [1] Shao-Horn, Y., et al., *Instability of Supported Platinum Nanoparticles in Low-Temperature Fuel Cells*. Top. Catal., 2007, **46**, p. 285-305.
- [2] Takahashi, I., et al., *Examination of the activity and durability of PEMFC catalysts in liquid electrolytes*, J. Power Sources, 2010, **195**, p. 6312-6322